Aldehyde Generators for Flavors

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Aldehydes are a potent class of flavor chemicals which make important contributions to the flavor effect in a wide range of fresh and prepared food products from fruits, spices, roasted and baked goods to vegetables.[1] As such, they are an integral part of the flavorist's palette for adding impact and character. Of the approximately 1750 items currently on the GRAS list, about 9 percent are either aldehydes and their corresponding acetals, or essential oils comprised mainly of aldehydes, such as Chinese Cassia (cinnamic aldehyde) or Litsea Cubeba (citral).

Difficulties in Use

One problem confronting the flavorist or food technologist when creating or utilizing flavors containing aldehydes, especially aldehydes such as acetaldehyde and benzaldehyde, is their relatively unstable nature compared to other common flavor components such as esters and alcohols.

The range of difficulties encountered with the aldehyde function is most aptly demonstrated in the case of acetaldehyde, which is reactive and highly volatile (boiling point 21°C). Acetaldehyde undergoes a number of oxidation and polymerization reactions to form acetic acid, paraldehyde, and other products. In addition, it can react with other flavor components to reduce or destroy its effect in a flavor. As a comparison, benzaldehyde and lauric aldehyde readily exhibit oxidation and trimer formation, respectively, to give benzoic acid in the one case (it is common to see the acid rapidly collect on the caps of bottles of benzaldehyde), and trimer formation in the other (where bottles of lauric aldehyde can rapidly go solid with trimer).

Stabilization Approaches

Early attempts to stabilize aldehydes consisted of acetal formation with simple lower alcohols such as methanol and ethanol, or cyclic acetal formation using propylene glycol and glycerin. These acetals can undergo hydrolysis to release the corresponding aldehyde; however, they additionally provide their own characteristic aroma (flavor or odor) which can distort the desired effect of the pure aldehyde. In the case of the cyclic acetals, their relatively slow hydrolysis rates can give a continually changing flavor profile. This changeable behavior can limit their usefulness in certain flavor applications where the acetal stabilization effect is desired but the true aldehyde flavor is needed immediately upon use.

More recent methods of providing stable aldehyde-releasing systems consist of either physical entrapment in various carbohydrate matrixes or various chemical derivitization methods, or a combination of both of these methods. Table I shows a cross-section of the many patented methods.

A recent article reviews the methods for protecting aldehydes by matrix entrapment such as spray-drying, dry-plating, melt-extruding, and freeze-drying.[3] In the article, Byrne and Sherman describe the various dry systems found in the patent literature where acetaldehyde is entrapped in a range of starches and sugars using the above methods. They conclude that physical entrapment systems of acetaldehyde are inferior in stability to the chemical system where acetaldehyde is generated from 1,2-di[(1′-ethoxy)eth-

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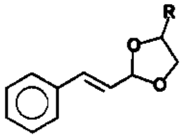
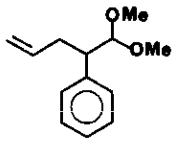
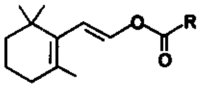
Table I

YEAR	U.S.PATENT	INVENTOR	ASSIGNEE	DESCRIPTION
1943 1943 1943	2,305,620 2,305,621 2,305,622	Kremers Kremers Kremers	General Foods General Foods General Foods	This group of patents covers the use of high molecular weight acetals, hemiacetals, ureides, ethylidene compounds, and carbamates.
1971	3,625,709	Mitchell	General Foods	Describes acetaldehyde carbohydrate complexes formed by reaction with chloride salts.
1974 1974	3,818,107 3,857,964	Yolles Yolles	Yolles/Brook Yolles/Brook	Cyclic acetals of aldehydes for sustained release in chewing gum. 
1974	3,829,504	Hall & Vock	IFF	Acetals of 2-or 3-phenyl pentenals which act as precursors for free aldehydes which alter the flavor of consumable materials. 
1977 1978	4,048,201 4,086,927	Pittet et al.	I.F.F.	Enol acetates which could serve as aldehyde generators for tobacco, chewing gum, and fruit flavors. 

(continued)

oxy]propane, FEMA 3534. Moreover, this chemical generator provides a high ratio of aldehyde per unit weight, which translates to a dry flavor system containing 10 percent of acetaldehyde. Comparatively, the physical entrapment systems have stable acetaldehyde loadings of about 2 percent.[3] Table II shows the aldehyde delivery content for various chemical derivatives.

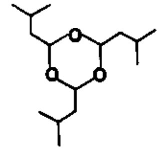
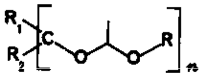
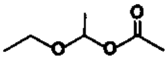
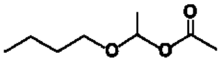
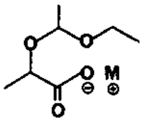
Generators, Synthetic vs. Nature

In nature, aldehyde generation occurs as the result of specific reactions. In the case of vegetables and fruits, cis-3-hexenal and other aldehydes are enzymatically generated.[4] In the aging of tea, enzymes are again involved to generate aldehydes.[5] Specific chemical reactions such as the Amadori rearrangement, the Maillard reaction and the Strecker degradation, occur during cooking, heating or roasting.[6] Such processes lead to the production of aldehydes and other flavorants. Examples are the roasting of cocoa beans[7] and meat.[8]

In order to be most effective, synthetic aldehyde generators should imitate natural systems. To accomplish this the following criteria should be met:

—the aldehyde should be generated as close to the time of use as possible
—the generating system should be sufficiently stable to release only at the time of use
—the generation should occur under the conditions of use
—a generator should not interfere with the desired flavor profile prior to the generation process
—the generator should not produce any coproducts which interfere with the flavor profile

(table 1 continued)

YEAR	U.S.PATENT	INVENTOR	ASSIGNEE	DESCRIPTION
1978 1980	4,093,752 4,191,785	Withycombe et al.	I.F.F.	Isovaleraldehyde trimer which is a potential generator for chewing gum, tobacco, and various flavors 
1981	4,280,011	DeSimone	PFW Hercules	Polylinear acetals as generators for foodstuff applications 
1981 1982	4,296,137 4,347,857	Boden	I.F.F.	1-ethoxy-1-acetoxyethane "which acts as a generator ...to yield acetaldehyde" in flavors and for tobacco. 
1981 1983	4,296,138 4,386,063	Boden	I.F.F.	1-butoxy-1-acetoxyethane for fixing acetaldehyde in grape flavors. 
1986	Pending	Byrne	PFW Hercules	Carboxylate salts of acetals as rapid aldehyde generators. 

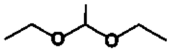
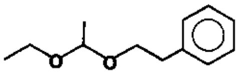
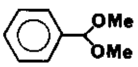
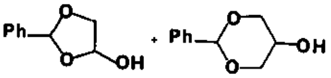
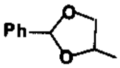
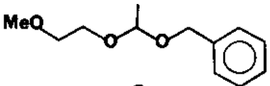
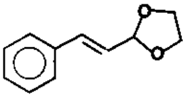
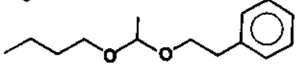
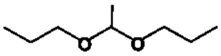
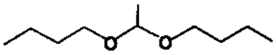
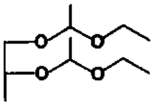
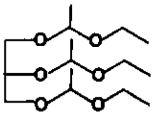
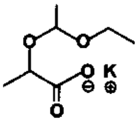
Review of Patented Systems

As Table I shows, a large effort in the aldehyde generator area has centered on acetaldehyde. This is due to acetaldehyde's importance in citrus, berry and other fruit flavors where it adds a "fresh" character.[9] The difficulty of employing acetaldehyde in dry flavors is due to its being highly volatile (bp 21°C) and oxidatively unstable under ambient conditions. As a result, it is quite difficult to entrap acetaldehyde in a matrix in the first place and, secondly, to provide a system where it remains protected. Many of the matrix systems in the literature describe intial acetaldehyde loadings of up to 7 percent; however, the stability of these systems under conditions found in prepared dry foods is quite poor. Moreover, the stable percentage of fixed acetaldehyde is seldom more than about 2 percent.[3]

The first attempt to use chemical derivatization, other than simple acetals, is described by Kremers.[10] These derivatives for the most part are either too stable for the desired release, generate undesirable side products, or have an interfering flavor. Mitchell's answer was to develop a physically entrapped acetaldehyde;[11] however, this system suffers from low aldehyde delivery levels and poor shelf life.

Yolles responded by use of cyclic acetals for sustained release in chewing gum.[12] Here, three levels of release are described: hydrolysis of the flavor acetal; diffusion through a polymeric matrix; and diffusion through an outer coating surrounding the flavor particle. This system is de-

Table II

FEMA #	%ACTIVE	NAME	STRUCTURE
2002	37	Acetaldehyde Diethyl Acetal	
2004	21	Acetaldehyde Phenethyl Propyl Acetal	
2128	70	Benzaldehyde Dimethyl Acetal	
2129	59	Benzaldehyde Glycerine Acetal	
2130	65	Benzaldehyde Propylene Glycol Acetal	
2148	21	Acetaldehyde Benzyl Beta Methoxyethyl Acetal	
2287	75	Cinnamic Aldehyde Ethylene Glycol Acetal	
3125	20	Acetaldehyde Penethyl Butyl Acetal	
COE 2342	30	Acetaldehyde Di-Propyl Acetal	
COE 2341	25	Acetaldehyde Dibutyl Acetal	
3534	40	1,2-Di[(1'-ethoxy)ethoxy] Propane	
3593	43	1,2,3-Tris[(1'-ethoxy)ethoxy] Propane	
3752	22	Potassium 2-[(1'-ethoxy) ethoxy]propanoate	

scribed as being particularly useful in chewing gums for generating cinnamic aldehyde (cinnamon). However, the amount of aldehyde generated is low in this system, and much of the acetal remains unhydrolyzed in the gum.[13]

In work similar to Yolles, Hall and Vock used acrylic acetals of 2- and 3-pentenals as precursors to the aldehydes, imparting a chocolate flavor at acidic pHs.[14]

Pittet reports certain enol acetates which are described as having utility in tobacco, chewing gum and fruit flavors.[15] Although the general intent voiced in the patent appears to be the use of the enol acetates as flavor chemicals in their own right, it appears that at low or high pH and with heat, the enol acetates would hydrolyze to the corresponding aldehydes. This would allow aldehydes to be generated in certain food systems where heating is utilized, such as in tobacco or in gelatin desserts. An analogous situation exists with the next patent, where Withycombe reveals the use of isovaleraldehyde trioxane as a flavor chemical on its own merit and disavows its having utility in relation as a isovaleraldehyde precursor.[16] While this is the case in cold flavor applications, in heated applications it appears that the reverse of the well-known aldehyde trimerization reaction takes place, generating the aldehyde. Such applications might be in baked goods and tobacco.

More recently, DeSimone reports the polylinear acetals are useful for generating aldehydes in foodstuffs where the acetals themselves and their hydrolysis co-products can be designed to have no interfering flavor of their own.[17] Additionally, these acetals release in cold acidic applications (dry beverage mixes) or under heating (gelatin desserts) to give a clean, uncontaminated aldehyde flavor effect.

Other examples are reported by Boden, who describes the usefulness of two acetaldehyde generators in tobacco and grape flavors.[18,19] However, these compounds suffer from their ability to react with other food ingredients as will be discussed later.

Table III

Type	% Stable Fix (after 1 year)
Melt-extruded	∿2%
Spray-dried	∿1.7
Colloidal-milled	∿1.5%
Freeze-dried	< 0.1%

Commercial Systems

While accurate marketing information about aldehyde delivery systems is scarce, several observations can be made. Of the patented systems described in Table I, the actual acetals that have been allowed as GRAS for use in the United States include several Yolles-type cyclic acetals, two DeSimone polylinear acetals, and one Byrne carboxylate salt acetal. One of the GRAS generators, FEMA 3534, has been incorporated into a spray-dried flavor,* which has found utility in dry beverage mixes and gelatin desserts. The widely offered matrix-encapsulated systems (see Table III) have found commercial acceptance mainly for beverage powders, and this only for the spray-dried acetaldehyde systems. The stable acetaldehyde fix for these systems is never greater than 2 percent where for our purposes "stable" is defined as the amount of aldehyde remaining after 12 months at ambient temperature and humidity.

GRAS Acetals

Table II shows a number of acetals potentially useful as aldehyde generators. One of the simplest precursors, acetal, FEMA 2002, has an ethereal odor of its own and is itself quite volatile. These factors mitigate against the use of acetal as a convenient generator. Similarly the other linear simple acetals, COE 2342 and COE 2341, would exhibit the same problems as would the co-products having their own interfering aroma. A number of cyclic acetals are on the GRAS list. These are usually made by reacting the aldehyde with either propylene glycol or glycerine. As a class, the cyclic acetals hydrolyze too slowly to be useful in most applications. Figure 1 exemplifies how slow the rates of these cyclic acetals are relative to the linear acetal, FEMA 3534. The mixed phenethyl and benzyl acetals, FEMA 2004, FEMA 2148 and FEMA 3125, can also serve as acetaldehyde generators, but either have their own strong aroma or their hydrolysis products would interfere with that of a pure aldehyde flavor. This would leave the remaining three acetaldehyde generators, FEMA 3534, 3593 and 3752, which have low, non-interfering odors, are relatively non-volatile, and upon hydrolysis do not give aroma interfering co-products. The hydrolysis products are flavor-neutral ethanol and propylene glycol in the case of FEMA 3534, or glycerine and ethanol for FEMA 3593. The hydrolysis schemes for FEMA 3534 and 3593 are shown in figure 2.

"Designer" Generators

Recent work has shown the significance of hydrolysis rates on the selection of an aldehyde generator.

As discussed previously the acyclic acetals hydrolyze faster than do the corresponding cyclic acetals. While cyclic acetals will find utility in heated applications (assuming that they meet all other criteria for a generator), acyclics will find greater use in ambient applications. For cold applications a new generator was designed (FEMA 3752).

In chemistry, if something acts as a catalyst to accelerate the rate of a reaction (hydrolysis), then incorporating this catalyst into the same molecule as the generator group will produce an even greater rate-enhancing effect. For the hydrolysis of acetals to aldehydes, acids act as catalysts. Incorporation of an acid into an acetal should accelerate the rate of hydrolysis; however, it might appear to be a futile effort as it would lead to premature hydrolysis of the acetal. But if the acid were itself protected until it was needed, then a successful catalyzed-generator molecule could

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*Aldemax is a trade name of Hercules/PFW.

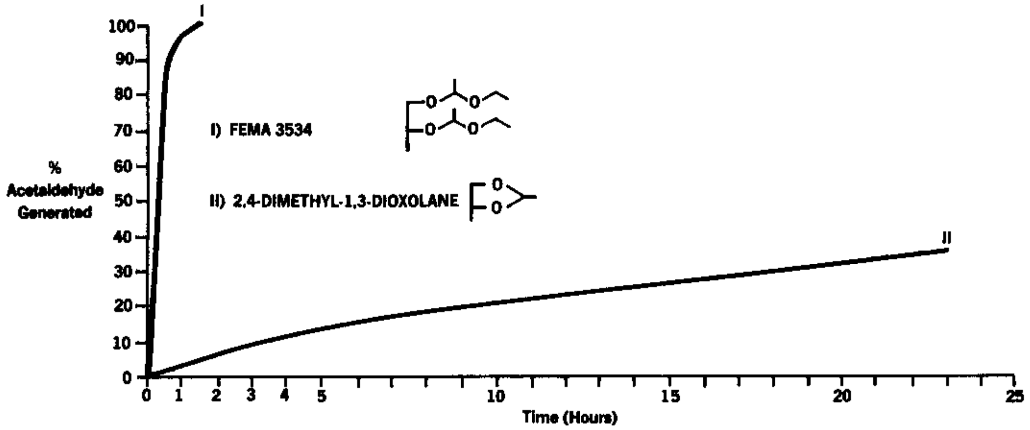

Figure 1. Hydrolysis of FEMA 3534 and 2,4-Dimethyl-1,3,-Dioxolane (pH 3.0, 25°C)

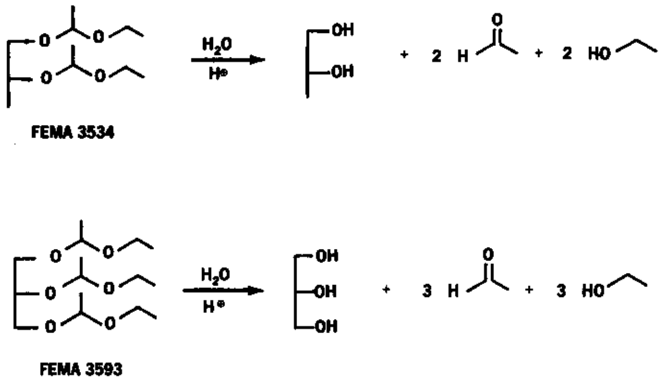

Figure 2

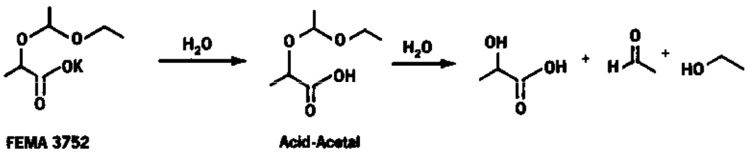

Figure 3

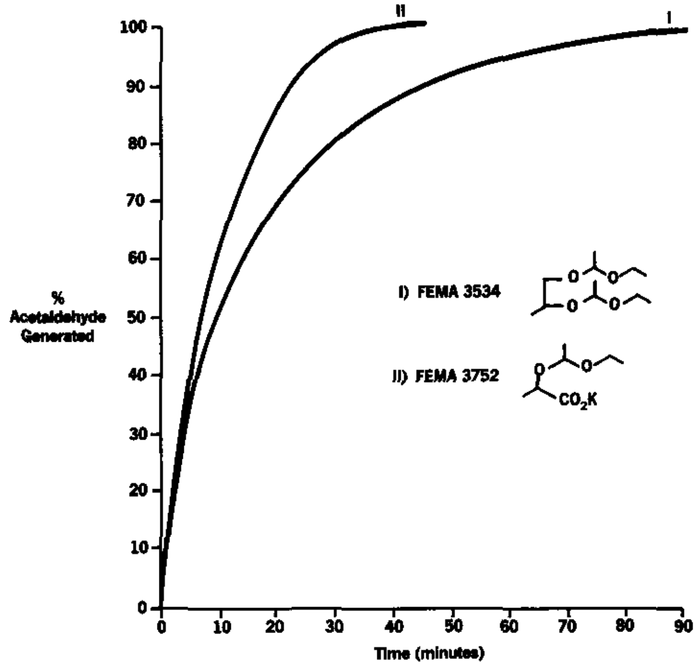

Figure 4. Hydrolysis of FEMA 3534 and FEMA 3752 (pH 3.0, 25°C)

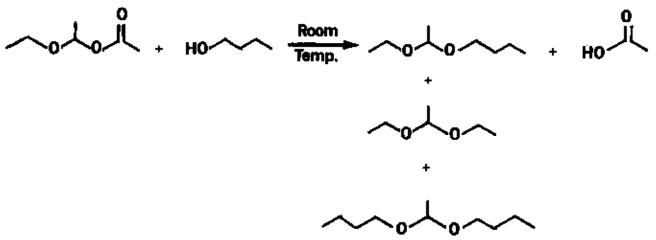

Figure 5

be fashioned. In the case of FEMA 3752, the lactic acid acetal is protected as a potassium salt. (See figure 3).

When FEMA 3752 is added to dilute aqueous solutions, the salt converts to the acid-acetal. The presence of the acid in the immediate vicinity of the acetal reaction site in the molecule internally catalyzes the rapid hydrolysis to acetaldehyde, ethanol and lactic acid. The rate enhancement is evident in figure 4.

Precautions for Use

Care must be exercised in selecting a generator since some are prone to decompose during spray-drying or during the compounding of flavors. For example, 1-ethoxy-1-acetoxyethane decomposes spontaneously when exposed to water, even atmospheric humidity. Additionally when compounded with various hydroxylic flavorants (alcohols and acids), it rapidly reacts to give a complex mixture of acetals (see figure 5).

The manner in which acetals are handled in liquid flavors and in dry formulations is also important. Even traditionally stable acetals can be prematurely hydrolyzed, or decomposed if subjected to high temperatures in the presence of moisture and acids. These unfavorable conditions may take place during flavor compounding, during formulation into a food, or inadvertently during warehouse storage. In such cases, the stability of an acetal becomes preeminent. Although a generator may be stable for its intended use in a food product, the method of preparation and packaging should accommodate for potenitally stressful situations such as blending, agglomeration, transport and storage.

Summary

The quest to deliver unstable aldehydes to food systems by the use of generators is being realized. With the proper generator, flavors can be created for use under conditions traditionally unfavorable to aldehydes. As in other derived systems it appears best to employ nature as a model and to design generators in the same way that nature produces flavors.

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